Synthesis of Bidentate Phosphorus Ligands for Heavy Metal Chelation

C'arra Miller
Grand Valley State University

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A current challenge faced by society is the increased implementation of more sustainable energy sources and the reduction of carbon-based energy sources. In addition, these sources must meet immediate energy demands and minimize any detrimental effects on the environment. One such favorable energy source is nuclear power. In the case of nuclear power, this method generates significant amounts of energy with minimal atmospheric emissions. Unfortunately, two major challenges limit its usage, which are the remediation and long term storage of nuclear waste, also referred to as spent nuclear fuel (SNF). The separation of SNF is in part due to the inability to separate lanthanides and long-lived radioactive actinides. Since both groups of heavy metals share similar oxidation states, chemical properties, and ionic radii, identifying optimal conditions for separating the two proves difficult. To address these challenges, a growing area of research has been focused on extraction techniques of SNF that are capable of separating rare-earth metals and recovering long-lived radioactive material.

Currently, there are separation methods that exist that are able to retrieve actinides and lanthanides, but issues concerning the recovery ratios and selective binding toward either lanthanides or actinides still remains. Two major separation techniques are the PUREX and the TRUEX processes. In the PUREX (i.e., Plutonium Uranium Recovery by Extraction) process, a tributylphosphine ligand in kerosene or dodecane solvent is used to extract lanthanide and actinide metals from an acidic aqueous solution. This process is useful for the removal of uranium and plutonium, but is inefficient at removing minor actinides from a nuclear waste solution. In the TRUEX (i.e., TRansUranium Extraction) process, the extracting agent consists of a mixed solvent system that includes the TBP ligand from the PUREX process and a CMPO ligand in kerosene or dodecane solvent. This mixed solvent system can extract transuranics and lanthanides from an acidic aqueous solution. Good recovery ratios of actinides were observed using this mixed extraction system, but recovery of the metals proved difficult due to the high nitric acid concentrations. In addition, the TRUEX process also extracts lanthanide metals, which can interfere with further treatment of the radioactive actinide ions.

Inspired by current extraction techniques and their ligands, our lab synthesized a series of monosubstituted and disubstituted cis-1,2-diphenylphosphineethylene (dppe) derivatives containing selenium and sulfur as soft donors. The structures of these ligands were confirmed via $^1$H NMR, $^{13}$C NMR, $^{31}$P NMR, and mass spectrometry. In addition, their coordination chemistry with platinum was investigated by $^{195}$Pt NMR and X-ray crystallography. The efforts of synthesizing these dppe derivatives are to study their metalation reactions with platinum(II) and lanthanum(III). If our efforts at coordinating these ligands are successful, obtaining crystal structures of the metal-ligand complexes via X-Ray crystallography will be the next goal.

*This scholar and faculty mentor have requested that only an abstract be published.